

A Facile Polyvinylpyrrolidone Assisted Solvothermal Synthesis of Zinc Oxide Nanowires and Nanoparticles and Their Influence on the Photovoltaic Performance of Dye Sensitized Solar Cell

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A facile polyvinylpyrrolidone (PVP) assisted solvothermal method was adopted to synthesis Zinc Oxide (ZnO) nanostructures. PVP was used as a capping agent as well as a nanoreactor to fabricate ZnO nanoparticles and ZnO nanowires by solvothermal reaction of zinc acetate in polyol medium. The influence of Zn (II)/PVP molar ratio on the size and morphology of ZnO was also investigated. The change in ZnO morphology from well-defined spherical nanoparticles to 1D-nanowire assembly upon varying Zn (II)/PVP molar ratio was observed by using SEM and TEM studies. 1D-ZnO nanowires based DSSC showed enhanced photovoltaic performance due to the absence of electron hopping that limited the electron transport in ZnO nanoparticles. The DSSC fabricated using ZnO nanowires as photoanode exhibited higher power conversion efficiency (PCE) of 1.81 % than that fabricated using ZnO nanoparticles (1.13 %) as photoanode.

Keywords: Wurtzite ZnO; ZnO Nanoparticles; ZnO Nanowires; Solvothermal synthesis; Polyvinyl pyrrolidone

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1. Introduction

Recent research activities in the field of the dye-sensitized solar cell (DSSC) have drawn great interest in improving its performance.¹⁻⁵ Being a crucial component, the photoanode material has a governing effect on overall photo-conversion efficiency of DSSC.⁶ Since, the first report by O'Regan and Grätzel on mesoporous TiO₂ based DSSC, many other semiconductors such as ZnO and SnO₂ have also been investigated in place of TiO₂ for DSSC.⁷⁻¹¹

ZnO possess high anisotropic growth compared to TiO₂, along with good intrinsic electrical and optical properties, which helps to achieve high electron mobility, high electron diffusion coefficient and easy separation of photogenerated electrons.^{12,13} However, TiO₂ based perovskite sensitized solar cell is still maintaining the record of the best photoconversion efficiency, which has now risen to 15.4%.^{14, 15} Despite, the higher electron mobility of ZnO, DSSC comprised of ZnO nanoparticles show lower photoconversion efficiency than that of DSSC comprised of TiO₂. Research efforts have been made to improve the performance of ZnO to use as DSSC photoanode.¹⁶⁻²⁰ It is evident from the studies that the interdependence of electron transport (τ_e) and electron lifetime(τ_n) is the reason for the poor efficiency of ZnO

nanoparticles based DSSC, which may be overcome by replacing the ZnO nanoparticles with 1D-ZnO nanostructures.^{21, 22} These observations show both the shape of ZnO material and its interconnections strongly influence the way that electrons are made to transport through the DSSC photoanode.²³

Thus, the structural control of 1D-ZnO nanostructure having a well-defined shape is still an important goal for improving the power conversion efficiency of DSSC. Several efforts have been directed towards the synthesis of 1D-ZnO nanostructures by various synthetic approaches.^{17, 24} Among them, liquid phase synthesis is more facile and reproducible for producing nanostructures with compositional homogeneity. Most of these synthesis process requires high temperature and use of stabilizers/surfactants for morphological control which increases the reaction complexity and causes the impurity in the products. Solvothermal liquid-phase synthesis process has led to the simultaneous precipitation of suitable precursors in high-boiling alcohols, which has been proven to be a promising green chemical approach for practical significance.²⁵ There have been reports on the synthesis of ZnO nanoparticles in different polyol media (ethylene glycol, diethylene glycol, 1,2-propanediol, etc. These polyol solvents act as complexing agent as well as a surfactant which adsorb on the surface of nanoparticles, thus preventing the aggregation of the nanoparticles.

We already demonstrated Polyvinylpyrrolidone(PVP) assisted solvothermal synthesis of nanostructured MgO and TiO₂ using ethylene glycol.^{26, 27} Here, ethylene glycol (EG) has been chosen to serve as a solvent as well as a reducing agent due to its relatively high boiling point (~197 °C) and high reducing capability. Besides, polyvinylpyrrolidone (PVP) was used exclusively as a capping agent. The power conversion efficiency of DSSC composed of the prepared TiO₂ is nearly close to

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that of the same fabricated with std. TiO_2 paste (Dye sol Ltd.) and higher than the same fabricated with P25 TiO_2 (Degussa) based photoanode.²⁷ These results have inspired to extend this PVP-assisted solvothermal process to prepare ZnO nanostructures for DSSC applications.

In the present investigation, we report an overall strategy of synthesizing ZnO nanoparticles and ZnO nanowires by a facile PVP assisted solvothermal process. The morphology, thermal behaviour and optical properties of the obtained ZnO nanostructures were investigated. Further, DSSCs were fabricated using ZnO nanoparticles and ZnO nanowires as photoanodes and their photovoltaic performances were studied in detail.

2. Experimental details

2.1 Materials

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.99%) and ethylene glycol (EG, 99.8 %) were procured from Sigma Aldrich. Polyvinylpyrrolidone (PVP, M. Wt. 130, 000) was purchased from AcrosOrganics. All the chemicals were used as received without further purification.

2.2 Synthesis of ZnO nanoparticles and ZnO nanowires

In the typical nanoparticles synthesis, 0.1mol of zinc acetate was taken in a round bottom flask containing 100 mL of EG. To this, PVP was introduced at different mole concentrations (0.001, 0.002, 0.003, and 0.004 mol) with constant stirring to know the effect of various mole ratios of Zn (II)/PVP on nanoparticles formation. These solutions were refluxed at 195 °C for 3 h. The precipitate was then collected by centrifugation. The residual PVP and EG were removed by washing with a copious amount of de-ionized water and ethanol. Finally, the precipitates were dried at 80 °C for 2 h under vacuum, followed by calcination at 350 °C for 2h to obtain ZnO nanoparticles. ZnO nanowires were prepared by following the same procedure by dissolving 1 mmol of zinc acetate and 0.2 mmol of PVP in 100 mL of EG.

2.3 Characterization

The thermal behaviour of ZnO precursors was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA) (Pyris Diamond, Perkin Elmer). The phase purity of the samples was evaluated by X-ray diffractometer (JEOL, Model: JDX) using nickel-filtered Cu-K radiation between 10 ° to 80 ° at 2 °/min.

Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of ZnO nanostructures. The respective nitrogen adsorption isotherms were recorded at 77 K using a surface analyzer (Micromeritics, Model: ASAP 2000).

The morphologies of ZnO nanostructures were investigated by using scanning electron microscope (JEOL, Model: JSM-840A, SEM) and High-resolution Transmission electron microscope (TEM) (Model: JEM 3010).

Photoluminescence (Model: Hitachi 850 fluorescence spectrophotometer) spectra of ZnO nanoparticles and ZnO nanowires were obtained using a Xe lamp (150 mW) as an excitation source at the excitation wavelength of 325 nm in between 350 and 600 nm.

2.4 Fabrication of DSSC

The ZnO pastes were prepared by mixing 30 wt.% of prepared ZnO nanostructures, 15 wt.% ethyl cellulose (binder), 50 wt.% terpineol (solvent) and 5 wt.% dibutyl phthalate (plasticizer) with intermittent sonication.

The prepared ZnO pastes were coated at the thickness of 10-12 μm

on the cleaned FTO glass substrates by the doctor-blade method. They were then sintered in a muffle furnace at 450 °C for 30 min to obtain ZnO photoanodes. The active area was 0.20 cm^2 . The fabricated ZnO photoanodes were immersed in the N719 dye for 24 h and rinsed with pure ethanol to remove the excess of dye. The Pt counter electrodes were fabricated by sintering the std. Pt paste (Dyesol Ltd.) coated FTO glass plates at 450 °C for 30 min. Finally, DSSCs were assembled by sandwiching each photoanodes and counter electrodes using thermal adhesive films (Surllyn, Dupont 1702, 60 μm -thick) by a hot press. The acetonitrile containing 0.5 M 1-butyl-3-methylimidazolium iodide, 0.05 M I_2 , 0.5 M LiI, and 0.5 M 4-tert-butylpyridine as the electrolyte was injected through the holes and then sealed with small squares of surllyn strip.²⁸

2.5 Photovoltaic performance of DSSC

The photovoltaic performance of the assembled DSSCs based on ZnO nanowire and ZnO nanoparticles are analyzed using the solar simulator having light intensity of 100 mW/cm^2 (AM 1.5) integrated with computer-controlled digital source meter (Keithley, Model: 2420). Three DSSCs were fabricated for each system and their average photovoltaic values were taken.²⁹

3. Results and Discussion

3.1 TG/DTA analysis

Fig. 1(a) shows the TG/DTA result of the ZnO precursor of nanoparticles (solid line) obtained using 0.1:0.002-mole ratio of Zn (II)/PVP. It is observed that the maximum weight loss occurs at about 330 °C. In the DTA curve, the endothermic peak at 117 °C corresponds to ~4.3 % of mass loss due to the removal of physically adsorbed EG and water and the exothermic peak at 330 °C corresponds to ~36.7 % of mass loss due to the degradation of EG and organic groups.³⁰ Further, there is no special mass loss observed from the above said temperature and the crystallization of the ZnO also starts at this temperature. Fig. 1(b) shows that there is no special difference in the mass loss of the ZnO precursor of nanowires in the first step from the TG and its corresponding endothermic peak in DTA curve (dashed line). From this figure, it is clearly seen that the exothermic peak corresponding to the degradation of EG and organic groups occurred at 322 °C in the DTA curve with the mass loss of ~36.1 % (dashed line).

3.2 XRD studies

The XRD patterns of ZnO products are obtained by calcination of

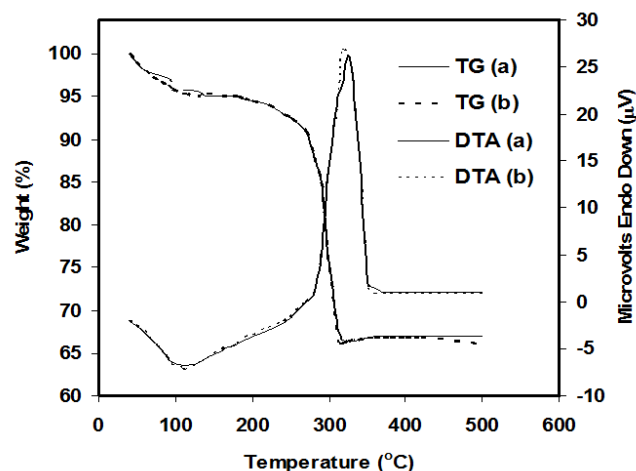


Fig. 1 TG/DTA curves of ZnO precursors of a) Nanoparticles (solid line) and b) Nanowires (dashed line).

various mole ratio of Zn(II)/PVP precursors at 350 °C. But only a representative XRD pattern for the mole ratio of 0.1/0.002 is shown in Fig. 2(a). This calcination temperature is quite consistent with the result of DTA. The high phase pure wurtzite ZnO nanoparticles with no impurity diffraction peaks are observed by calcinating the precursor sample at 500 °C for 2h [Fig. 2(b)]. These diffraction patterns are well matched with the standard diffraction pattern of wurtzite-type ZnO (JCPDS card No.36-1451, $a = 3.249 \text{ \AA}$, and $c = 5.026 \text{ \AA}$). Their average particles size is calculated by using following Scherrer's formula and they are 14.6, 12.8, 47.0 and 81.0 nm respectively. The increase in the particle size at its higher concentration may be due to the adverse effect of the capping agent, as summarized in Table1.

The sharp diffraction peaks of the ZnO nanowires (Fig. 3) that are collected at the temperature of 500 °C for 2h are well indexed to the JCPDS card No. 36-1451 of wurtzite-type ZnO structure with lattice constant values of $a = 3.249 \text{ \AA}$ and $c = 5.026 \text{ \AA}$.

3.3 BET surface area analysis

Table 1 summarizes the specific surface area of ZnO nanostructures. High surface area value of 121.2 m²/g is obtained for the PVP ratio of 0.002 mole than other concentrations. The marked difference in the surface area was attributed to the choice of the PVP content that altered the energetic of the solvothermal process.

3.4 SEM and TEM studies

SEM image confirms that the synthesized ZnO nanoparticles have single-phase primary particles as evident from Fig. 4(a). It shows that the ZnO nanoparticles obtained from the 0.1/0.002 mole ratio of Zn (II)/PVP calcined at 500 °C for 2 h are spherical in shape. The abnormal agglomeration of grains did not appear in the calcined product. The average diameter obtained from the SEM picture is less than 20 nm. Some particles exhibited a diameter higher than 20 nm. This may be due to the agglomeration of ZnO nanoparticles. The formation of ZnO nanoparticles is further confirmed by TEM studies.

The HR-TEM image confirms that ZnO nanoparticles obtained by calcinating the sample at 500 °C for 2h are nearly spherical in shape of size ~12 nm (Fig. 4(b)). Fig. 4(c) presents the lattice fringes with the spacings of 2.60 and 2.47 representing the (002) and (101) planes, respectively for hexagonal wurtzite ZnO nanoparticles. Fig. 4(d) shows the particles size histogram of prepared ZnO nanoparticles corresponding to the TEM image shown in Fig. 4(b). The size distribution was characterized by means of particle size of ~12.5 nm, relatively narrow distribution, although the size of some large particles is in the range between 12-16 nm as seen in the corresponding Fig. 4(d). The mean crystal size has a good relationship with the crystallite size (12.8 nm) obtained from the XRD pattern (Fig. 2). Eventually, PVP changes the properties of the polyol product. As the capping agent, it

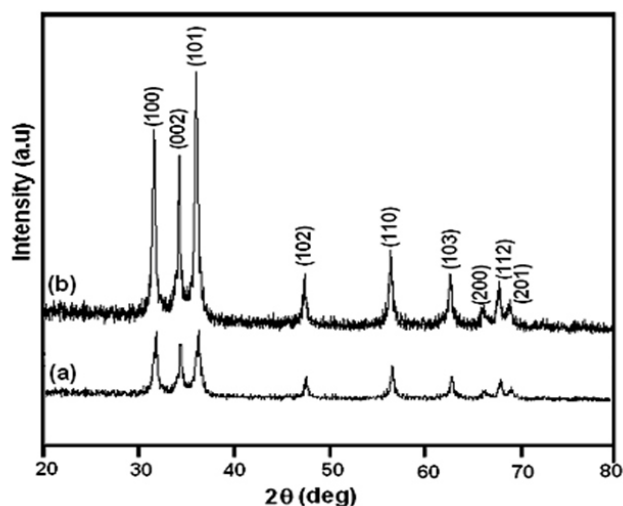


Fig. 2 XRD patterns of zinc oxide nanoparticles obtained by calcination of the precursor at (a) 350 °C and (b) 500 °C for 2 h.

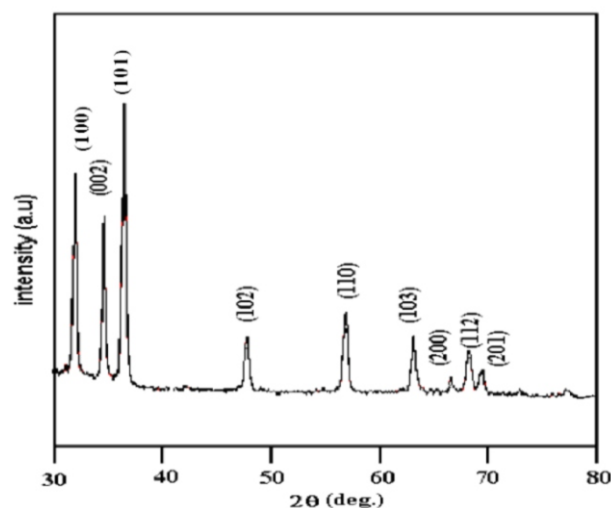


Fig. 3. XRD pattern of ZnO nanowires at 500 °C for 2h.

Table1. The specific surface area and particles size of the prepared ZnO products obtained from the solvothermal process.

Mole ratio		Specific surface area (m ² /g) ^a	Crystallite size (nm) ^b	Particles size (nm) ^c
Zn(CH ₃ COO) ₂	PVP			
0.1	0.001	91	14.6	14.8
0.1	0.002	121	12.8	12.5
0.1	0.003	71	47.2	47.0
0.1	0.004	53	81.3	81.0

^a From BET analysis; ^b From XRD Scherrer's formula; ^c From TEM analysis.

reduces the particles size in the nanoscale without any agglomeration in the prepared ZnO product.

As seen in Fig. 5(a&b), the ZnO nanowires exhibited 1D nanostructure with no amorphous layer at the starting to end tip of the wires. From the SEM image Fig. 5 (a), it is found that the diameter and length of the ZnO nanowires obtained are 10-30 nm (average diameter ~22 nm) and 20 μm , respectively. TEM image Fig. 5(b) clearly designates that ZnO nanowires have a uniform width along their entire length. Fig. 5(c) shows the lattice fringes with a spacing of 0.519 nm and the arrow indicating the growing direction. The inset Fig. 5 (d) shows the selected-area electron diffraction (SAED) pattern confirming the lattice spacing and the c axis [0001] of the single-crystalline ZnO nanowires. However, the ZnO nanowires become shorter (data not shown here) and transformed into bulk ZnO structure upon calcination at 600 $^{\circ}\text{C}$ for 2 h.

3.5 Photoluminescence spectra

The photoluminescence spectra (Fig. 6) show that ZnO nanoparticles and nanowires exhibited UV emission at 382 nm and 380 nm, respectively, implying their wide band gap. The green light emission observed at 520 nm and 517 nm, respectively, is attributed to the presence of ionized oxygen vacancy. The recombination of this oxygen vacancy with the photogenerated hole causes the green emission.³¹

As evident from the SEM and HR-TEM images, the morphology of wurtzite ZnO nanostructure is changed with changing in the molar concentrations of Zn (II)/PVP. The zinc acetate precursor solution at 0.1 mole yields spherical morphology, whereas, the 0.002-mole results in wire like morphology. This demonstrated that the average diameter of ZnO nanowires strongly depends on the precursor concentration. Further, as the capping agent, PVP influences the nucleation kinetics and subsequent growth. At higher concentration, the presence of PVP

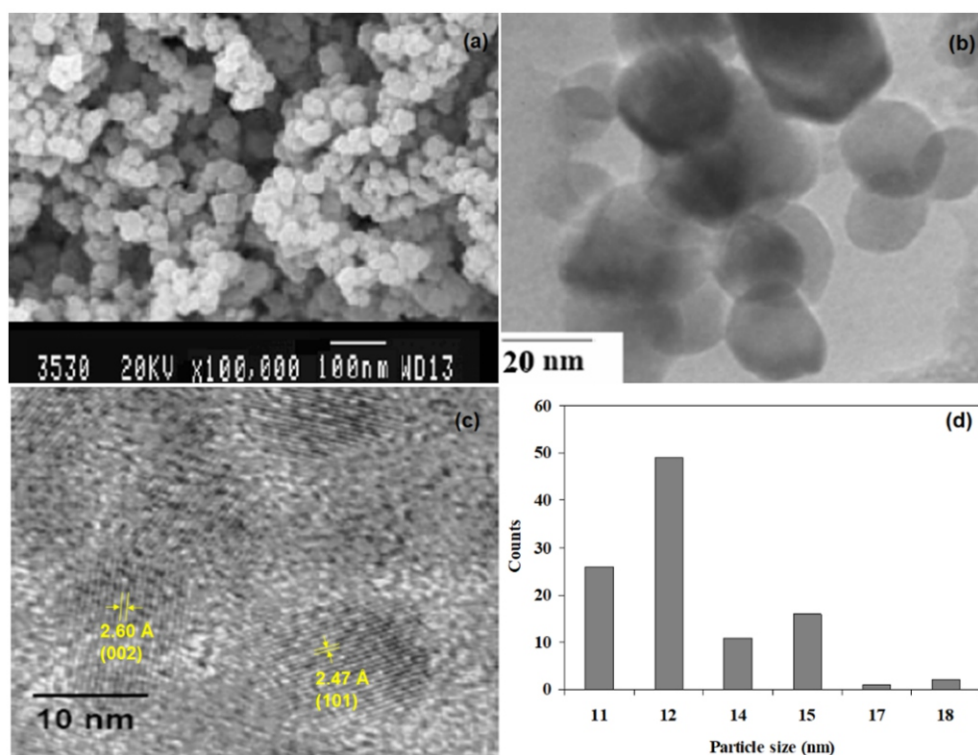


Fig. 4 (a) SEM image; (b) TEM image; (c) HR-TEM image; (d) Particles size histogram of ZnO nanoparticles obtained from the solvothermal process.

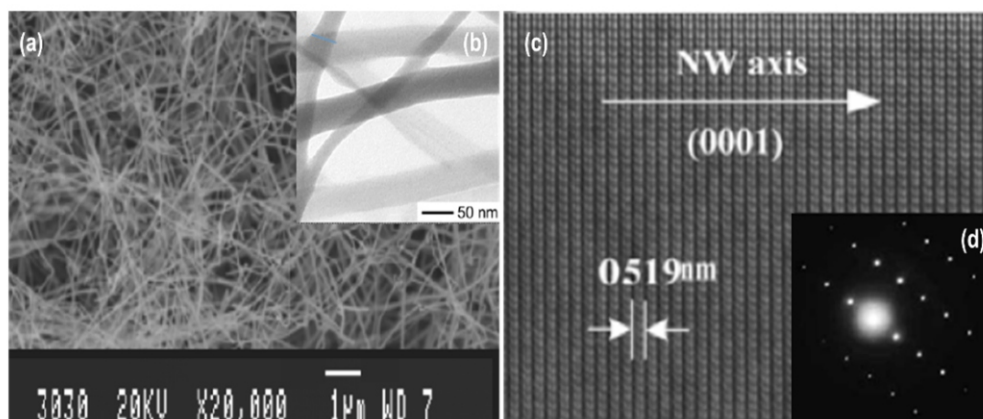


Fig. 5 (a) SEM image; (b) HR-TEM image; (c) HR-TEM image; (d) Selected-area electron diffraction (SAED) pattern of ZnO nanowires obtained from the solvothermal process.

slows down the growth of larger particles, whereas the growth remains almost same for small particles. Thus, the PVP plays a critical role in obtaining nanoparticles of uniform size and shape. However, the interaction between the PVP molecules become more significant at lower molar concentration. This favours the formation of nanowires with controlled length and diameter.

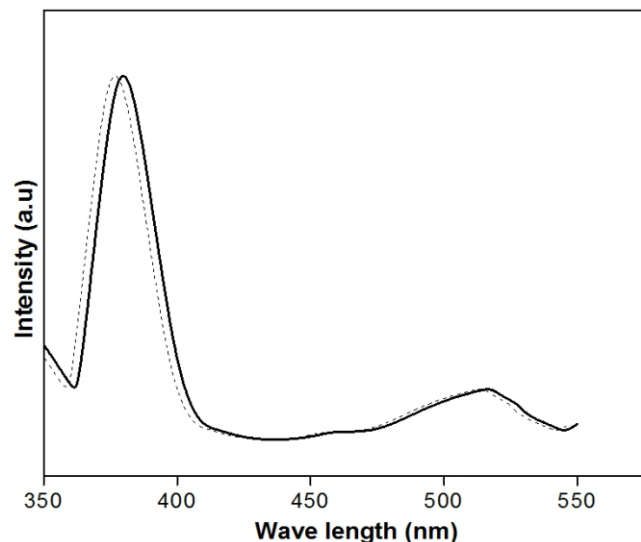


Fig. 6 Photoluminescence spectra of ZnO nanoparticles (solid line) and ZnO nanowires (dashed line).

3.6 Photovoltaic performance studies

Fig. 7 shows the photocurrent density-voltage (J-V) curves of DSSCs fabricated with ZnO nanowires and ZnO nanoparticles based photoanodes and their corresponding parameters are given in Table 2. It shows that the DSSC fabricated using ZnO nanowires as the photoanode exhibits the PCE of 1.81 % which is higher than that

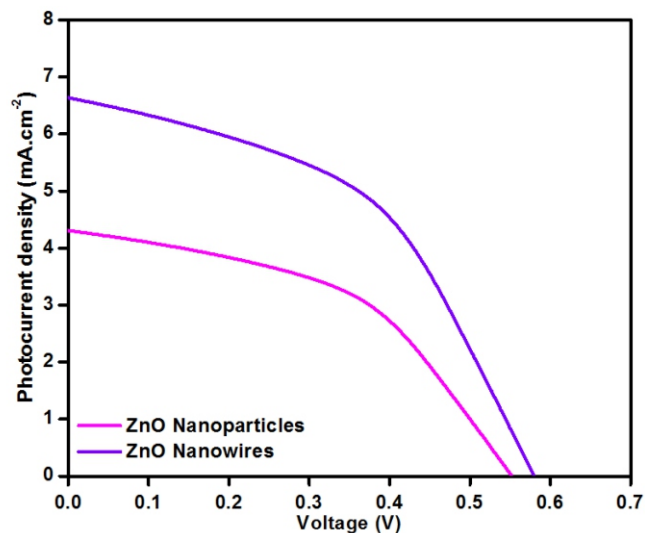


Fig. 7 Photocurrent density-voltage characteristics of DSSCs fabricated with (a) ZnO Nanowires and (b) ZnO nanoparticles based photoanodes.

Table 2 Photovoltaic parameters of DSSCs fabricated with (a) ZnO nanowires and (b) ZnO nanoparticles based photoanodes.

Photoanode	V_{oc} (V)	J_{sc} (mA.cm ⁻²)	FF	η (%)
ZnO Nanoparticles	0.55	4.31	0.475	1.13
ZnO Nanowires	0.58	6.64	0.469	1.81

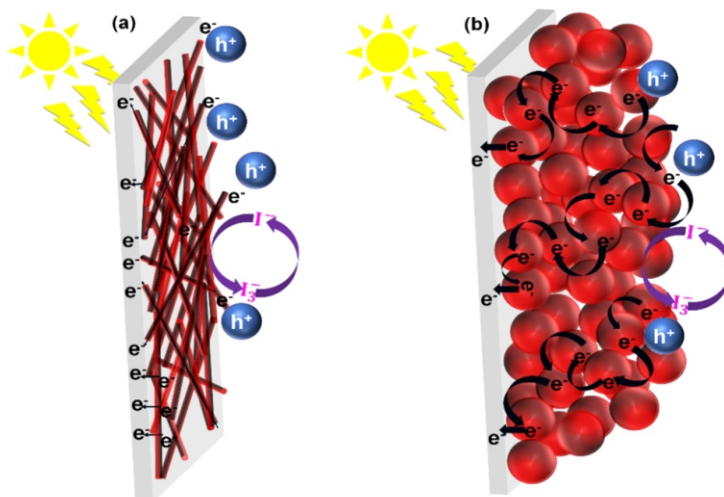


Fig. 8 Schematic illustration of photo-excited electrons transport in (a) ZnO Nanowires and (b) ZnO Nanoparticles based photoanodes.

Table 3 Comparison of photovoltaic performance of DSSC based on prepared ZnO nanowires with reported ZnO nanowires based DSSCs.

S.No.	Photoanode	Synthesis method	PCE (%)	Ref.
1.	ZnO Nanowires	Microwave - assisted hydrothermal method	1.55	34
2.	ZnO Nanowires	Chemical solution method	0.812	35
3.	ZnO Nanowires	Chemical solution method	1.52	36
4.	ZnO Nanowires	Chemical solution method	1.49	37
5.	ZnO Nanowires	Chemical solution method	1.45	38
6.	ZnO Nanowires	PVP assisted solvothermal method	1.81	This work

fabricated using the ZnO nanoparticles-based photoanode (1.13 %). This is due to electron hopping events that limit electron transport in the case of ZnO nanoparticles based photoanode. The prepared ZnO nanowires exhibited superior PCE than the other reported ZnO nanowires (Table 3).

The possibility of grain boundary between the nanoparticles reduced the chemical potential (or charge transport energy) contact which makes the time delayed charge transport via hopping events along the nanoparticles. But, in the case of ZnO nanowires, the continuum chemical potential contact (due to the absence of grain boundaries) leads to chemically driven carrier transport which can be explained by unified Einstein's diffusion-mobility model.³² Here, the electron transport enhancement in ZnO nanowires swiftly allows the photogenerated electrons before the recombination started.³³ Hence, the electron transfer rate in the ZnO nanowires is higher than ZnO nanoparticles which are schematically illustrated in Fig. 8. This allows a higher photocurrent (J_{sc}) with an improved photoconversion efficiency for the DSSC fabricated with ZnO nanowires based photoanode.

4. Conclusion

High phase pure wurtzite ZnO nanoparticles and ZnO nanowires were successfully prepared by PVP assisted solvothermal process. During the thermal decomposition of the precursor, crystallization started at 330 °C and a well-defined polycrystalline powder was obtained at 500 °C for 2h. Especially, ZnO nanoparticles have a crystallite size of 12-16nm and its average surface area was 121.2 m²/g. The change in morphology and size of the ZnO were examined under various Zn(II)/PVP mole ratio and addressed in the present study. The characteristic UV emission at 382 and 380 nm and a green emission at 520 and 517 nm were observed for the prepared ZnO nanoparticles and ZnO nanowires, respectively. The highest PCE of 1.81 % was achieved for DSSC fabricated using ZnO nanowires as photoanode than that of ZnO nanoparticles based photoanode (1.13 %). This is due to the better electron mobility offered by ZnO nanowires.

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Conflict of Interest

The authors declare no conflict of interest.

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